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(56) Documents cited

**GB 1575457 A EP 0498043 A EP 0471937 A
EP 0471936 A EP 0073488 A2 WO 85/05626 A1
JP 010239707 A US 4684682 A**

(58) Field of search

**UK CL (Edition K) C3K KEB KEC KEF KEZ
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(54) **Flame-retardant polymeric material**

(57) Flame-retardant properties are conferred on styrenic polymers by compounding the polymers with a blend of:

(a) red phosphorus

and (b) a water-insoluble phosphorus compound, e.g. melamine phosphate, melamine pyrophosphate, ammonium polyphosphate or ethylene diamine phosphate. The styrenic polymer may be a high-impact polystyrene, a styrene/butadiene copolymer, an acrylonitrile/butadiene/styrene terpolymer, a styrene/butadiene/styrene terpolymer or a styrene/acrylonitrile copolymer.

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FLAME-RETARDANT POLYMERIC MATERIAL

This invention relates to a method for the production of a flame-retardant polymeric material and to a material obtained by means of the said method.

Red phosphorus and phosphorus-containing compounds are known, individually, as being capable of conferring flame-retardant properties on some polymeric materials (eg. polyamides), though not on others (eg. styrene-based polymers and some olefinic polymers). For each polymer to be treated, there has been found to be a "critical" level of flame-retardant additives, above which flammability of the polymer can in fact be enhanced and below which no acceptable degree of flame-retardancy can be attained.

We have, unexpectedly, found that a blend of red phosphorus with a phosphorus- containing compound leads to an effective and economic flame-retardancy of styrenic polymers.

Accordingly, the present invention provides a method for the production of a flame-retardant styrenic polymer, wherein said polymer is compounded with a flame-retardant additive and said additive comprises a blend of

- (a) red phosphorus and
- (b) a substantially water-insoluble phosphorus- containing compound.

The present invention also provides a flame-retardant styrenic polymer made by the method described in the immediately-preceding paragraph.

The constituent (b) of the blend may be, for example, melamine phosphate, melamine pyrophosphate, ammonium polyphosphate or ethylene diamine phosphate.

Suitably, the polymer may be compounded with from 0.5% to 15% (preferably from 2% to 10% and especially from 5% to 10%) by weight of (a) and from 0.5% to 50% (preferably from 2% to 20% and especially from 5% to 10%) by weight of (b). Wherever "percentage by weight" is referred to in this specification and claims, the quantities are related to the weight of the polymer.

The polymer may be a thermoplastics homopolymer, copolymer, terpolymer or mixed polymer.

Examples of polymers which may be used in the practice of the present invention include high-impact polystyrene (HIPS), styrene/butadiene copolymers, acrylonitrile/butadiene/styrene (ABS) and styrene/butadiene/styrene (SBS) terpolymers, or a styrene/acrylonitrile (SAN) copolymer.

Compositions according to the present invention may also include other conventional ingredients typically used in the manufacture of plastics materials, such as heat stabilisers, light stabilisers, anti-oxidants, anti-static agents, pigments, fillers, lubricants, plasticisers, impact strength modifiers, coupling agents and processing aids.

Preferred embodiments of the present invention will be illustrated, merely by way of example, as follows:

In Examples 1 to 3, powdered polystyrene (High Impact Grade Neste SB 735) was processed in 2Kg-batches with the indicated additives and blends. Processing was carried out in a Betol Twin-Screw Extruder at 240°C.

Strips of the extruded material, of thickness ranging from 1/32 to 1/4 inch, were subjected to the flammability test prescribed in American National Standard UL-94 V and the Limiting Oxygen Index (LOI) test prescribed in ASTM D2863-77.

Three examples illustrating the invention are given in TABLE 1 below as EXAMPLES 1 to 3. COMPARATIVE EXAMPLES 1 and 2 show the effect of red phosphorus alone and a red phosphorus-melamine blend respectively on the flammability of polystyrene:

TABLE 1

Ex.	Additive % by wt	LOI %O ₂	UL-94V (a)			
			1/4"	1/8"	1/16"	1/32"
1	red P 6.9% melamine phosphate 8.1%	23.2	V-0	V-0	V-2	V-2
2	red P 6.9% melamine pyrophosphate 8.1%	23.3	V-0	V-2	V-2	NR
3	red P 10% ammonium polyphosphate 10%	23.6	V-0	V-0	V-2	V-2
COMP. EX. 1	red P 15%	23.0	V-0	NR	NR	NR
COMP. EX. 2	red P 9% melamine 6%	23.2	NR	NR	NR	NR

(a) Flammability results are shown as:

or
V-0
V-1, V-2
NR

Non-burning
Self-extinguishing
Not Rated

A further three examples illustrating the invention are given in TABLE 2 below as EXAMPLES 4 to 6. COMPARATIVE EXAMPLES 3 to 5 show the effect of red phosphorus alone on the relevant polymers.

In Examples 4 to 6, a red phosphorus - melamine phosphate blend was evaluated in three styrenic polymers.

The polymer grades used were as follows:

High-Impact Polystyrene (HIPS) - BP 4230 grade

Acrylonitrile/butadiene/styrene (ABS) - Lucky 151 grade

Styrene/acrylonitrile (SAN) - Enichem Kostil AF1-2000PA grade

In these examples 500g batches were processed on a Prism laboratory twin-screw extruder. Moulded specimens of the extruded materials were tested as in Examples 1 to 3, and the results are shown below in TABLE 2:

TABLE 2

Ex.	Additive % by wt	Polymer	LOI %O ₂	UL-94V (a)			
				1/4"	1/8"	1/16"	1/32"
4	red P 6.9% melamine phosphate 8.1%	HIPS (BP4230 grade)	23.5	V-0	V-0	V-2	V-2
5	red P 6.9% melamine phosphate 8.1%	ABS (Lucky 151 grade)	23.2	V-0	V-2	V-2	V-2
6	red P 6.9% melamine phosphate 8.1%	SAN (Enichem Kostil AFI-2000 PA grade)	23.9	V-0	V-2	V-2	V-2
COMP. EX. 3	red P 15%	HIPS (BP 4230 grade)	22.7	V-0	NR	NR	NR
COMP. EX. 4	red P 15%	ABS (Lucky 151 grade)	22.8	V-0	NR	NR	V-2
COMP. EX. 5	red P 15%	SAN (Enichem Kostil AFI-2000 PA grade)	22.1	V-1	V-2	V-2	V-2

(a) Flammability results are shown as:

or V-0
V-1, V-2
NR

Non-burning
Self-extinguishing
Not Rated

H1030.

CLAIMS (GB)

1. A method for the production of a flame-retardant styrenic polymer, wherein said polymer is compounded with a flame-retardant additive and said additive comprises a blend of
 - (a) red phosphorus and
 - (b) a substantially water-insoluble phosphorus- containing compound.
2. A method according to Claim 1, wherein (b) is melamine phosphate.
3. A method according to Claim 1, wherein (b) is melamine pyrophosphate.
4. A method according to Claim 1, wherein (b) is ammonium polyphosphate.
5. A method according to Claim 1, wherein (b) is ethylene diamine phosphate.
6. A method according to any one of Claims 1 to 5, wherein said polymer is compounded with a blend comprising from 0.5% to 15% by weight of (a) and from 0.5% to 50% by weight of (b), relative to the weight of said polymer.
7. A method according to Claim 6, wherein said blend comprises from 2% to 10% by weight of (a) and from 2% to 20% by weight of (b).
8. A method according to Claim 6 or 7, wherein said blend comprises from 5% to 10% by weight of (a) and from 5% to 10% by weight of (b).

9. A method according to any of Claims 1 to 8, wherein said polymer is a thermoplastics polymer, copolymer, terpolymer or mixed polymer.
10. A method according to Claim 9, wherein said polymer is a high-impact polystyrene, a styrene/butadiene copolymer, an acrylonitrile/butadiene/styrene terpolymer, a styrene/butadiene/styrene terpolymer, or a styrene/acrylonitrile copolymer.
11. A method for the production of a flame-retardant styrenic polymer, substantially as hereinbefore described with reference to any one of the Examples.
12. A flame-retardant styrenic polymer made by the method of any one of the preceding claims.

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Patents Act 1977
Examiner's report to the Comptroller under
Section 17 (The Search Report)

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Relevant Technical fields

(i) UK Cl (Edition K) C3K (KEB, KEC, KEF, KEZ)

(ii) Int Cl (Edition 5) C08K; C08L

Search Examiner

B J BALDOCK

Databases (see over)

(i) UK Patent Office

(ii) ONLINE DATABASES: WPI

Date of Search

13 OCTOBER 1992

Documents considered relevant following a search in respect of claims

1-12

Category (see over)	Identity of document and relevant passages		Relevant to claim(s)
X	GB 1575457	(GENERAL ELECTRIC) see Claims 1, 6, 7, 10, 11, 14, 15 page 2 lines 32-36, page 3 lines 1-40, Examples 16, 17	1, 9, 10
X, P	EP 0498043 A	(FREUDENBERG)	1, 4, 9, 10
X, P	EP 0471937 A	(FREUDENBERG)	1, 4, 9, 10
X, P	EP 0471936 A	(FREUDENBERG)	1, 4, 9, 10
X	EP 0073488 A2	(MONTEDISON) see whole document	1, 4, 5
X	WO 85/05626 A1	(PLASCOAT) see Claims 1, 3 page 3 lines 3, 4, 9, 21, 22	1, 2, 4, 9, 10
X	US 4684682	(GENERAL ELECTRIC) see Claims 1, 2, Examples 16, 17	1, 9, 10
X	JP 010239707 A	(HITACHI) see WPI Accession No:- 89-320896/44	1, 9, 10

Category	Identity of document and relevant passages	Relevant to claim(s).

Categories of documents

X: Document indicating lack of novelty or of inventive step.

Y: Document indicating lack of inventive step if combined with one or more other documents of the same category.

A: Document indicating technological background and/or state of the art.

P: Document published on or after the declared priority date but before the filing date of the present application.

E: Patent document published on or after, but with priority date earlier than, the filing date of the present application.

&: Member of the same patent family, corresponding document.

Databases: The UK Patent Office database comprises classified collections of GB, EP, WO and US patent specifications as outlined periodically in the Official Journal (Patents). The on-line databases considered for search are also listed periodically in the Official Journal (Patents).

1. The first part of the paper discusses the importance of the study of the history of the United States. It is argued that the study of history is essential for understanding the present and for shaping the future. The author emphasizes that history is not just a collection of facts, but a way of thinking about the world.

2. The second part of the paper discusses the role of the individual in history. It is argued that individuals play a crucial role in shaping the course of history, and that their actions can have far-reaching consequences. The author emphasizes that individuals are not just passive recipients of history, but active participants in it.